13. Polyhedral hydroborates can be made by the "B—H condensation" route. Show how the general equation for this process applies to the synthesis of $B_6H_6^{2-}$ on page 1012. $NaB_{11}H_{14}$ can be prepared by the "B—H condensation" method starting with either B_2H_6 or $B_{10}H_{14}$ and other appropriate materials. Write a balanced equation to depict this synthesis.

14. Table 18-4 lists two carborane anions belonging to the *nido* series. Using the structural classification formulas developed earlier in the chapter, show that their *nido* classification is correct.

15. It was said that the "dsd" mechanism in Figure 18-13 cannot account for the conversion of *meta*-carborane to *para*-carborane. Prove that this is indeed true.

16. Tell what reagents would be used in the following reactions:
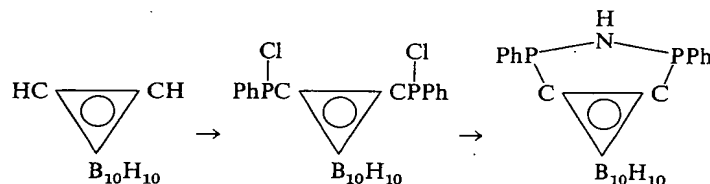
17. Write out a method for the synthesis of the following compound.
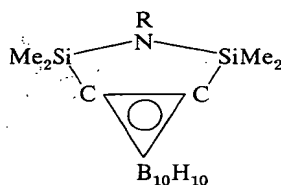
18. If the compound $(\eta^5\text{-}C_5H_5)CoB_4C_2H_6$ is to be prepared by the direct insertion method, with which carborane would one begin and what are the possible structures of the product?

19. Compounds **40** and **42** are synthesized by direct insertion into $B_3C_2H_5$. Discuss the bonding in these compounds. (Hint: refer back to the discussion of bonding in **17**.)

METAL-METAL BONDS AND METAL CLUSTERS[113-118]

Until about fifteen years ago very few compounds having metal-metal bonds were known or confirmed, save a few bimetallic compounds such as the mercury(I) halides. Since then, however, numerous compounds having a bond between at least

[113]D. L. Kepert and K. Vrieze in "Comprehensive Inorganic Chemistry," J. C. Bailer, Jr., H. J. Emeleus, R. Nyholm, and A. F. Trotman-Dickenson, eds., Pergamon Press, New York (1973), Chapter 47 in Volume 4.
[114]F. A. Cotton, *Chem. Soc. Revs.*, **4**, 27 (1975); *Acc. Chem. Res.*, **2**, 240 (1969).
[115]M. C. Baird, *Prog. Inorg. Chem.*, **9**, 1 (1968).
[116]R. B. King, *Prog. Inorg. Chem.*, **15**, 287 (1972).
[117]B. R. Penfold, "Stereochemistry of Metal Cluster Compounds," in "Perspectives in Structural Chemistry," J. D. Dunitz and J. A. Ibers, eds., John Wiley and Sons, New York (1968), Volume 2.
[118]P. Chini, G. Longoni, and V. G. Albano, *Adv. Organometal. Chem.*, **14**, 285 (1976).

two metals have been reported, and representative of this now important class are octachlorodirhenate(2−) [$Re_2Cl_8^{2-}$][113,119,120] with a quadruple Re—Re bond, the cluster R—$CCo_3(CO)_9$ (4),[121,122] and the organometallic chromium compound 43 with a triple Cr—Cr bond.[123]
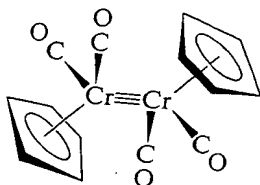
43

Just like the boron hydrides, metal clusters can be organized according to structural types. As seen in Table 18-5, there are bridged and unbridged compounds with simple metal-metal bonds—with orders ranging from 1 to 4—as well as triangular, tetrahedral, and octahedral clusters. A few other types, including an example of a cubic cluster, are mentioned in Table 18-5.

Understanding of the structures of compounds with metal-metal bonds has recently increased to the point where some generalizations can be made:

a) Unlike the boron hydrides, smaller metal clusters are usually not electron deficient, and the edges of metal cluster polyhedra can frequently be considered as normal two-electron bonds. There are, of course, exceptions, chiefly among the six-atom clusters to be discussed below.

b) The position of a metal in the Periodic Table, its oxidation state, and the attached ligands are important in determining the number and type of metal-metal bonds. Organometallic compounds with metal-metal bonds are common to almost all of the transition metals. On the other hand, metal halides with M—M bonds are based only on elements earlier in the second and third transition metal series.

The second of these observations can be explained by arguments based on valence orbital size. In general, as the oxidation state of a metal increases, or as Z^* increases, the valence orbitals contract. Such contraction should improve the ability of these orbitals to overlap. However, overlap between contracted orbitals on two metals can be effective only if the internuclear distance is shortened, and there are two factors opposing a decrease in M—M distance: (i) increasing atomic core repulsions, and (ii) increasing ligand-ligand repulsions. Core repulsions are disproportionately higher for 3d than for 4d or 5d metals, so metals in the first transition series do not form metal-metal bonds in higher oxidation states. However, in the low oxidation states characteristic of organometallic compounds, the first transition series metals are able to form metal-metal bonds.

BINUCLEAR COMPOUNDS

Some of the most thoroughly studied compounds of Class I-Al (see Table 18-5) are [Re_2Cl_8]$^{2-}$ and [Mo_2Cl_8]$^{2-}$ and their derivatives (Figure 18-15). The preparation

[119] The three main papers concerning the [Re_2Cl_8]$^{2-}$ ion are:
a. Preparation: F. A. Cotton, N. F. Curtis, B. F. G. Johnson, and W. R. Robinson, Inorg. Chem., 4, 326 (1965).
b. Structure: F. A. Cotton and G. B. Harris, Inorg. Chem., 4, 330 (1965).
c. Bonding: F. A. Cotton, Inorg. Chem., 4, 334 (1965).
[120] For the latest work on [Re_2Cl_8]$^{2-}$ and similar compounds, the following is a leading reference: F. A. Cotton and E. Pedersen, Inorg. Chem., 14, 383 (1975).
[121] B. R. Penfold and B. H. Robinson, Acc. Chem. Res., 6, 73 (1973).
[122] D. Seyferth, Adv. Organometal. Chem., 14, 97 (1976).
[123] J. Potenza, P. Giordano, D. Mastropaolo, and A. Efraty, Inorg. Chem., 13, 2540 (1974).

TABLE 18–5
METAL CLUSTERS

Cluster Type	Compound	Structure/Properties	Reference
I. Binuclear			
A. Homoatomic			
1. Inorganic unbridged	$[Re_2Cl_8]^{2-}$	quadruple bond; Figure 18–16	a
2. Inorganic bridged	$Mo_2(NMe_2)_6$	triple Mo—Mo bond	b
	$Cr_2(O_2CCH_3)_4 \cdot 2H_2O$	quadruple Cr—Cr bond	c
	$[Mo_2(SO_4)_4]^{3-}$	quadruple Mo—Mo bond	d
3. π-Organometallic bridged	$(\eta^5\text{-}C_5H_5)_2V_2(CO)_5$		e
4. π-Organometallic unbridged	$(\eta^5\text{-}C_5Me_5)_2Cr_2(CO)_2$	triple Cr—Cr bond	f
	$(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_6$	single Cr—Cr bond	g
5. σ-Organometallic unbridged	$Mo_2(CH_2SiMe_3)_6$	triple Mo—Mo bond	h
	$Mn_2(CO)_{10}$	single Mn—Mn, D_{2d} symmetry	i
6. σ-Organometallic bridged	$Fe_2(CO)_9$	single Fe—Fe bond, three CO bridges	j
	$(C_{10}H_{18})_2Fe_2(CO)_4$	Fe—Fe double bond with two Me_3C—$C \equiv C$—CMe_3 bridges	k
B. Heteroatomic	$(\eta^5\text{-}C_5H_5)Co(CO)_2 \cdot HgCl_2$	Co functions as a Lewis base	l
	$(\eta^5\text{-}C_5H_5)W(CO)_3SnMe_3$		m
	Me_3Ge—$Mn(CO)_5$		n
II. Trinuclear	$[Re_3Cl_{12}]^{3-}$	dark red, structure **48**	a
	$Fe_3(CO)_{12}$	green-black, structure **50**	a
	$H_2Os_3(CO)_{10}$	46 valence electrons; unsaturated with apparent Os—Os double bond; OsH_2Os bridging unit.	o
	$(\eta^5\text{-}C_5H_5)_3Ni_3(CO)_2$	green; triply bridging CO's on each side of metal triangle; paramagnetic	p
III. Tetranuclear			
A. Four metal atoms	$[(\eta^5\text{-}C_5H_5)Fe(CO)]_4$	dark green, structure **52**	a
	$H_2Ru_4(CO)_{13}$	red	q
	$H_2Re_4(CO)_{14}$	deep red; 58 valence electrons; unsaturated with two Re—Re double bonds	r
	$Co_4(CO)_{12}$	black — note color change with increasing metal weight; 9 terminal CO + 3 bridging CO for Co and Rh, all terminal for Ir; structures **53** and **54**	s, t
	$Rh_4(CO)_{12}$	red	
	$Ir_4(CO)_{12}$	yellow	
B. Three metal atoms + one hetero-atom	RC—$Co_3(CO)_9$	deep purple; all CO terminal; structure **55**	u
	$SCo_3(CO)_9$	black	v
IV. Five-atom cluster	$[M_2Ni_3(CO)_{16}]^{2-}$	(M = Cr, Mo, W) one of the very few 5-metal atom clusters; trigonal bipyramid with 3 Ni in equatorial plane	w

TABLE 18–5 (Continued)

Cluster Type	Compound	Structure/Properties	Reference
V. Six-atom cluster	$CFe_5(CO)_{15}$	square pyramid of $Fe(CO)_3$ units with carbide ion in square base; structure **59**	x
	$Rh_6(CO)_{16}$	black; 6 $Rh(CO)_2$ units in octahedral arrangement with 4 facial CO's; structure **56**	y
	$Os_6(CO)_{18}$	bicapped trigonal prism of Os	z
VI. Seven-atom cluster	$[(Nb_6Cl_{12})Cl_6]^{3-}$		aa
	$CRh_6(CO)_{17}$	deep red; C atom in center of Rh_6 octahedron	bb
VII. Eight-atom cluster	$Ni_8(CO)_8(\mu_4\text{-PPh})_6$	a cube of Ni atoms with 2-electron Ni—Ni bonds along each edge; a PPh ligand symmetrically caps each face; structure **65**	cc
VIII. Nine-atom cluster	$[Pt_9(CO)_9(\mu_2\text{-CO})_9]^{2-}$	structure **58**	dd

[a] See text.

[b] M. Chisholm, F. A. Cotton, B. A. Frenz, and L. Shive, *Chem. Commun.*, 480 (1974).

[c] F. A. Cotton, B. G. DeBoer, M. D. LaPrade, J. R. Pipal, and D. A. Ucko, *J. Amer. Chem. Soc.*, **92**, 2926 (1970).

[d] F. A. Cotton, B. A. Frenz, and T. R. Webb, *J. Amer. Chem. Soc.*, **95**, 4431 (1973).

[e] F. A. Cotton, B. A. Frenz, and L. Kruczynski, *J. Amer. Chem. Soc.*, **95**, 951 (1973).

[f] J. Potenza, P. Giordano, D. Mastropaolo, and A. Efraty, *Inorg. Chem.*, **13**, 2540 (1974).

[g] R. D. Adams, D. E. Collins, and F. A. Cotton, *J. Amer. Chem. Soc.*, **96**, 749 (1974).

[h] F. Huq, W. Mowat, A. Shortland, A. C. Skapski, and G. Wilkinson, *Chem. Commun.*, 1079 (1971).

[i] L. F. Dahl and R. E. Rundle, *Acta Cryst.*, **16**, 419 (1963).

[j] H. M. Powell and R. V. G. Evans, *J. Chem. Soc.*, 286 (1939).

[k] K. Nicholas, L. S. Bray, R. E. Davis, and R. Pettit, *Chem. Commun.*, 608 (1971).

[l] I. M. Nowell and D. R. Russell, *J. Chem. Soc., A*, 817 (1971).

[m] T. A. George and C. D. Turnipseed, *Inorg. Chem.*, **12**, 394 (1973).

[n] A. Terzis, T. C. Strekas and T. G. Spiro, *Inorg. Chem.*, **13**, 1346 (1974).

[o] H. Kaesz, *Chemistry in Britain*, **9**, 344 (1972).

[p] M. R. Churchill and R. Bau, *Inorg. Chem.*, **7**, 2606 (1968).

[q] D. B. W. Yawney and R. J. Doedens, *Inorg. Chem.*, **11**, 838 (1972).

[r] R. Saillant, G. Barcelo, and H. Kaesz, *J. Amer. Chem. Soc.*, **92**, 5740 (1970).

[s] C. H. Wei, *Inorg. Chem.*, **8**, 2384 (1969).

[t] S. H. H. Chaston and F. G. A. Stone, *J. Chem. Soc., A*, 500 (1969).

[u] B. R. Penfold and B. H. Robinson, *Acc. Chem. Res.*, **6**, 73 (1973).

[v] C. H. Wei and L. F. Dahl, *Inorg. Chem.*, **6**, 1229 (1967); C. E. Strouse and L. F. Dahl, *J. Amer. Chem. Soc.*, **93**, 6032 (1971).

[w] J. K. Ruff, R. P. White, Jr., and L. F. Dahl, *J. Amer. Chem. Soc.*, **93**, 2159 (1971).

[x] E. H. Braye, W. Hübel, L. F. Dahl, and D. L. Wampler, *J. Amer. Chem. Soc.*, **84**, 4633 (1962).

[y] E. R. Corey, L. F. Dahl, and W. Beck, *J. Amer. Chem. Soc.*, **85**, 1202 (1963).

[z] R. Mason, K. M. Thomas, and D. M. P. Mingos, *J. Amer. Chem. Soc.*, **95**, 3802 (1973).

[aa] F. W. Koknat and R. E. McCarley, *Inorg. Chem.*, **13**, 295 (1974).

[bb] A. Sirigu, M. Bianchi, and E. Benedetti, *Chem. Commun.*, 596 (1969).

[cc] L. D. Lower and L. F. Dahl, *J. Amer. Chem. Soc.*, **98**, 5046 (1976).

[dd] P. Chini, G. Longoni, and V. G. Albano, *Adv. Organometal. Chem.*, **14**, 285 (1976).

of the two octahalodimetallates is illustrative of methods used to produce metal-metal bonds in general.[124,125] That is, a higher valent compound is reduced to a lower valent species wherein metal-metal bond formation is more favorable.

The chief feature of interest with regard to these ions is their molecular geometry and what this implies about the bonding between the metals (Figure 18–16).[125,126] Two aspects of their structures are especially important: (i) in both cases the Cl atoms

[124] See ref. 119a.

[125] J. V. Brencic and F. A. Cotton, *Inorg. Chem.*, **9**, 346, 351 (1970).

[126] See ref. 119b.

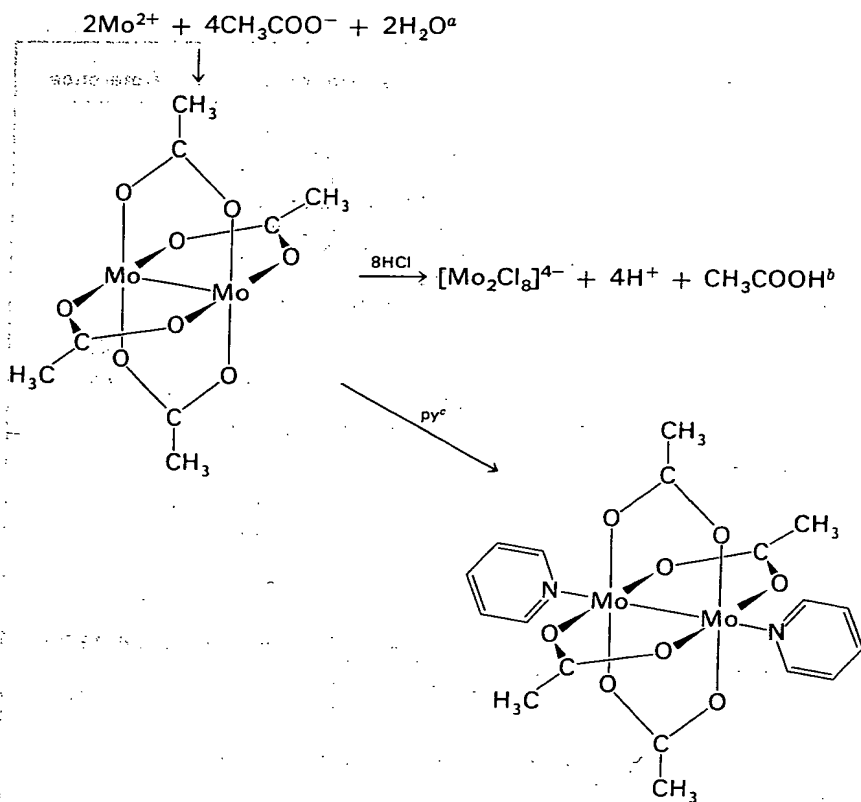$$2Mo^{2+} + 4CH_3COO^- + 2H_2O^a$$

$$\xrightarrow{8HCl} [Mo_2Cl_8]^{4-} + 4H^+ + CH_3COOH^b$$

Figure 18–15. The preparation and chemical properties of $[Re_2Cl_8]^{2-}$, $[Mo_2Cl_8]^{2-}$, and related compounds. References: [a] T. A. Stephenson, E. Bannister, and G. Wilkinson, *J. Chem. Soc.,* 2538 (1964). [b] J. V. Brencic and F. A. Cotton, *Inorg. Chem.,* **9**, 346 (1970). [c] F. A. Cotton and J. G. Norman, Jr., *J. Amer. Chem. Soc.,* **94**, 5697 (1972). [d] F. A. Cotton, N. F. Curtis, B. F. G. Johnson, and W. R. Robinson, *Inorg. Chem.,* **4**, 326 (1965). [e] F. A. Cotton, C. Oldham, and R. A. Walton, *Inorg. Chem.,* **6**, 216 (1967). [f] F. A. Cotton, W. R. Robinson, R. A. Walton, and R. Whyman, *Inorg. Chem.,* **6**, 929 (1967). [g] F. A. Cotton and E. Pedersen, *Inorg. Chem.,* **14**, 383 (1975).

are eclipsed, and (ii) both have a considerably shorter M—M distance [Re—Re = 2.24 Å and Mo—Mo = 2.14 Å] than in the metals themselves [Re = 2.714 Å and Mo = 2.725 Å]. Both of these features were recognized very early as being due to quadruple M—M bonds! To account for this, the following formalism may be adopted: The $d_{x^2-y^2}$ orbitals on the two metals are utilized for bonding to Cl⁻ ions. This leaves four orbitals—d_{z^2}, d_{xz}, d_{yz}, and d_{xy}—and the four electrons on each Re³⁺ (d^4). The σ bond between the metals derives from overlap of the d_{z^2} ao's, and the d_{xz} and d_{yz} orbitals form two π bonds. Finally, overlap of the d_{xy} orbitals on the two metals forms a δ bond (Figure 18–16). The new result is a quadruple bond with a bond strength estimated at 300 to 400 kcal/mole! Although the δ component is thought to be the weakest portion of the bond, it is of course just this component that dictates the eclipsed configuration.[127,128]

The bonding scheme outlined above means that there will be a d_{z^2} LUMO (44)

$$----\ \text{(z)}\ C_4\ \text{axis}$$
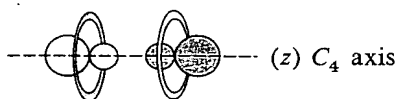
44

[127] The bonding in the rhenium salt has been described in two papers:
a. See ref. 119c.
b. F. A. Cotton and G. B. Harris, *Inorg. Chem.,* **6**, 924 (1967).
[128] J. G. Norman, Jr., and H. J. Kolari, *J. Amer. Chem. Soc.,* **97**, 33 (1975). This is a complete mo calculation that confirms the results of the earlier, more qualitative calculations.

$$8Cl^- + 2ReO_4^- + 8H^+ + 2PO_2^{3-\ d}$$

$[Re_2(SCN)_8]^{2-} \xleftarrow{8SCN^-\ f}$

$[Re_2Cl_8]^{2-}$

$\xrightarrow{\underset{HBF_4}{(CH_3CO)_2O^e}}$

$E_{\frac{1}{2}} = -0.840$
$(vs.\ SCE)^g$

$[Re_2Cl_8]^{3-}$

$\Delta \mid H_3CCOOH$
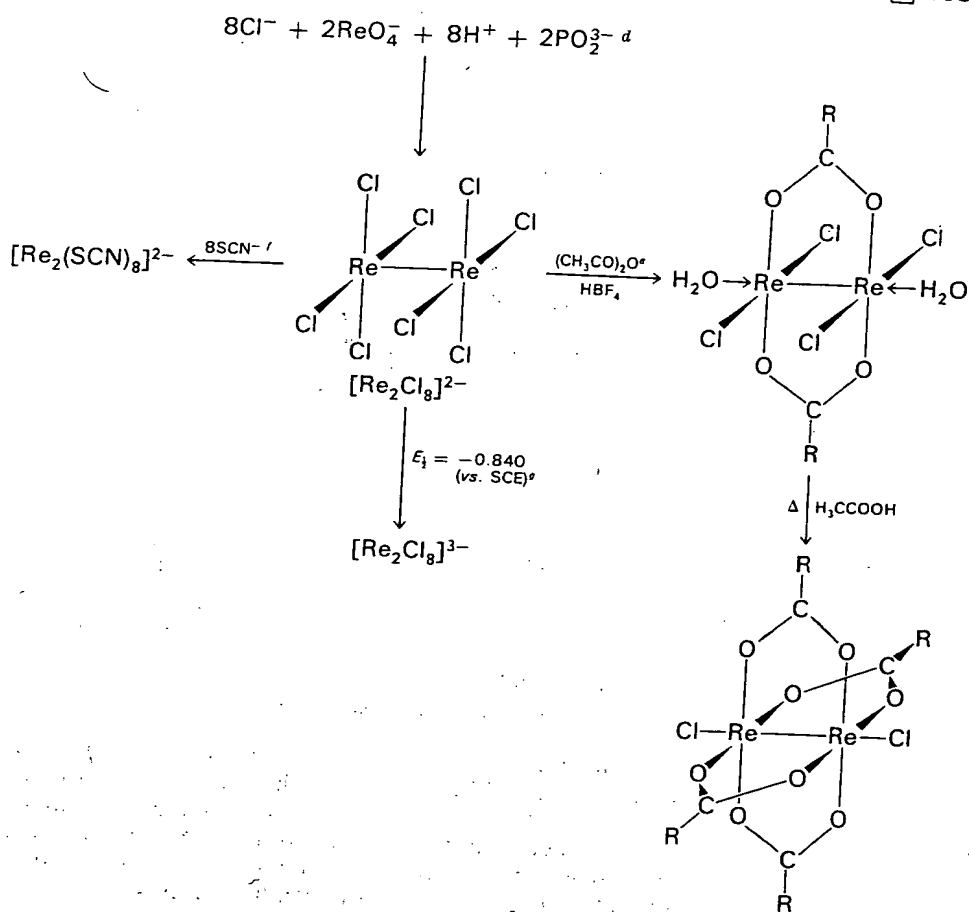
Figure 18-15. (Continued).

available for adduct formation. Therefore, it is not surprising that a molecule such as $Mo_2(O_2CR)_4(py)_2$ can be prepared (see Figure 18-15).[129] The further significance of this diadduct is that the Mo—Mo bond is lengthened by only 0.039 Å [from 2.080 Å in $Mo_2(O_2CCF_3)_4$ to 2.129 Å in the diadduct] and that the Mo—N bond (2.548 Å) is much longer than the Mo—O bond (2.116 Å).[130] These facts suggest that the metals

[129] Recall the Lewis acid behavior of I_2 (Chapter 5, p. 210), where a base can interact with an analogous p_z LUMO.

[130] F. A. Cotton and J. G. Norman, *J. Amer. Chem. Soc.*, **94**, 5697 (1972).

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Figure 18-16. (A) The structure of the $[Re_2Cl_8]^{2-}$ ion, and (B) a sketch showing the formation of a δ bond in $[Re_2Cl_8]^{2-}$ by overlap of the metal d_{xy} orbitals. [Reprinted with permission from F. A. Cotton and G. B. Harris, *Inorg. Chem.*, **6**, 924 (1967). Copyright by the American Chemical Society.]
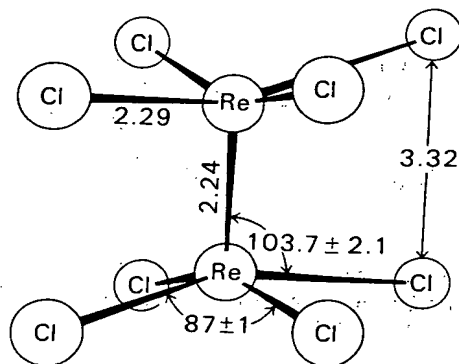

(A)
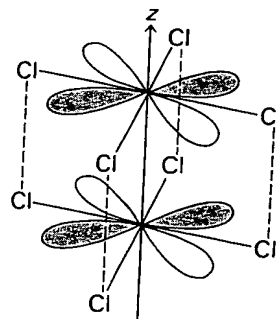
(B)
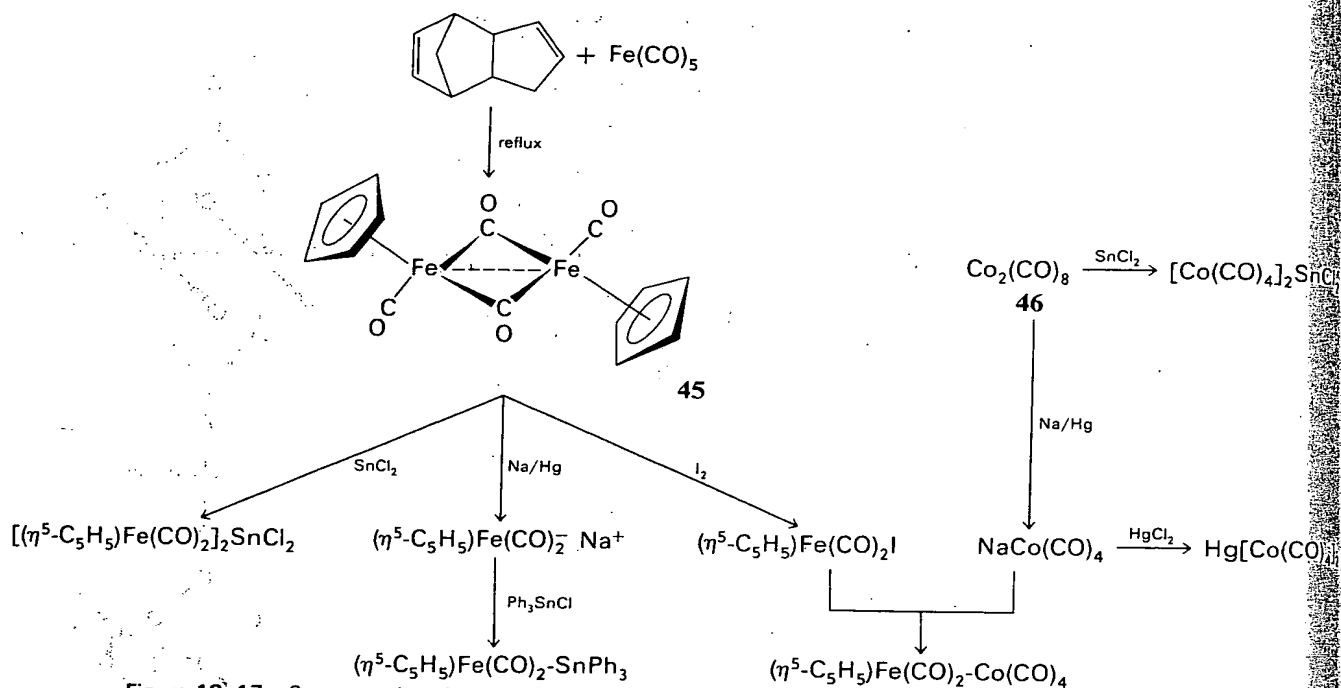
Figure 18-17. Some reactions leading to the formation of metal-metal bonds.

prefer to maintain their strong interaction rather than trade off any bond strength for a more "normal" Mo—N bond. This, of course, follows directly from the fact that it is a $d\sigma^*$ mo that is occupied by the pyridine lone pairs.

In general, there are probably more organometallic compounds having metal-metal bonds than there are of the type just discussed. More than likely this comes as a result of the fact that organometallic compounds are formed only by metals in low oxidation states, a factor that leads to greater net valence orbital availability as discussed earlier (p. 1027). Furthermore, at the moment there appear to be more straightforward synthetic methods available for organometallic compounds than for compounds such as the M—M bonded metal halides. For example, the organometallic compounds 45 and 46 in Figure 18-17 may be cleaved with sodium amalgam to give their respective mono-metal anions, and these anions may then react with a metal halide to give a host of unique compounds.

In addition to organometallic compounds with simple σ bonds between the same or different metals, there are those with multiple bonds. For example, reaction of 5-acetyl-1,2,3,4,5-pentamethylcyclopentadiene with $Cr(CO)_6$ gives 43,[131] a green, air-stable compound with a Cr—Cr triple bond.[132]
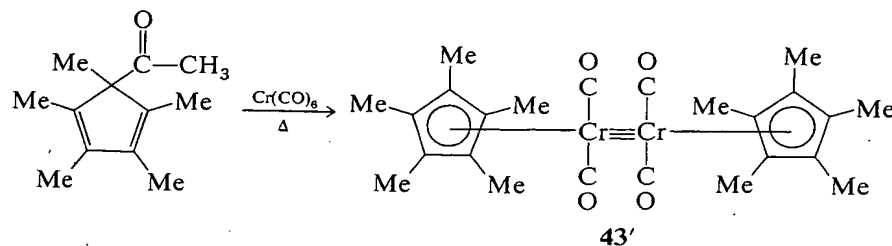
As might reasonably be expected, the Cr—Cr distance of 2.280 Å in 43 is significantly shorter than the Cr—Cr bond distance in 47 (3.281 Å), the latter clearly having only a single Cr—Cr bond.[133]

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[131] R. B. King and A. Efraty, *J. Amer. Chem. Soc.*, 94, 3773 (1972).
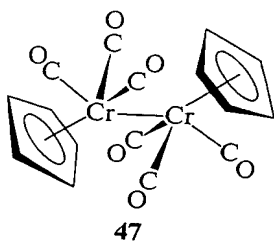[132] See ref. 123.
[133] R. D. Adams, D. E. Collins, and F. A. Cotton, *J. Amer. Chem. Soc.*, 96, 749 (1974).

47

However, the Cr—Cr distance in **43** is also shorter than the quadruple metal-metal bond in $Cr_2(O_2CCH_3)_4 \cdot 2H_2O$ (2.362 Å) (see Figure 18–15 for the Mo analog). The apparent conclusion that can be drawn from these comparisons is that metal-metal bond lengths cannot always be relied upon to reflect accurately the bond order; as discussed earlier, bond lengths are a compromise between attractive M—M forces and ligand-ligand repulsions.

THREE-ATOM CLUSTERS

Three metal atoms may form a chain or a triangular arrangement. However, in contrast to the *sp* block elements, the triangle appears to be the more favorable for transition metals; even in clusters with more than three metal atoms, the polyhedral faces are triangular just as in the boron hydrides. Numerous clusters containing three metals in a triangular arrangement are known, and among the most systematically studied are $[Re_3Cl_{12}]^{3-}$, its derivatives, and $Fe_3(CO)_{12}$ and its Ru and Os analogs.

The dark red salt of empirical formula $CsReCl_4$ is prepared by the following sequence of reactions:[134,135]

$$2\,Re + 5\,Cl_2 \rightarrow 2\,ReCl_5$$

$$ReCl_5 \xrightarrow{\Delta} ReCl_3 + Cl_2$$

$$ReCl_3 + CsCl \xrightarrow{HCl} CsReCl_4$$
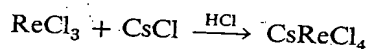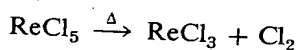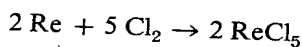
X-ray crystallography showed, however, that it is not the simple tetrahedral ion $ReCl_4^-$, but rather the trimeric ion $[Re_3Cl_{12}]^{3-}$ **(48)**.[136] The chief structural feature of interest is the Re—Re bond distance of 2.47 Å in the triangulated compound. This is somewhat longer than the quadruple bond in $[Re_2Cl_8]^{2-}$ (2.24 Å), but it is considerably shorter than the simple single bond in $(OC)_5Re—Re(CO)_5$. The Re—Re bond length in **48** may be explained by postulating a double bond between the rhenium atoms.

48
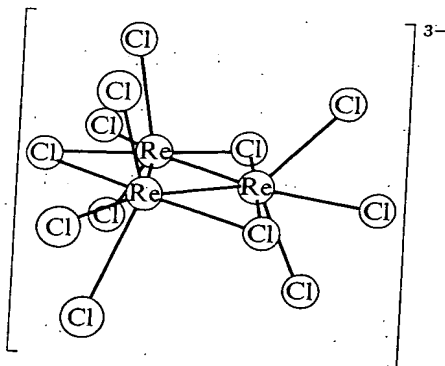
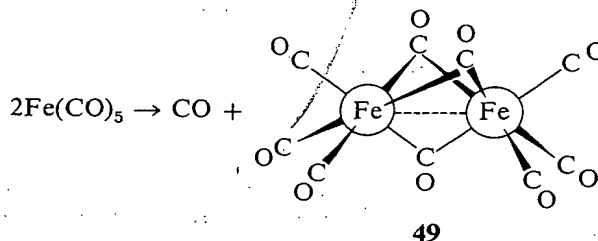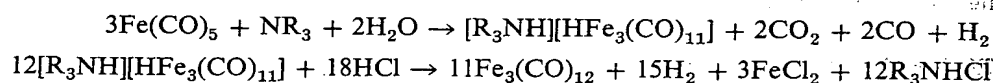[134] L. C. Hurd and E. Brimm, *Inorg. Syn.*, **1**, 180 (1939).
[135] W. Geilman and F. W. Wrigge, *Z. Anorg. Allgem. Chem.*, **223**, 144 (1935).
[136] J. A. Bertrand, F. A. Cotton, and W. A. Dollase, *Inorg. Chem.*, **2**, 1166 (1963).

Photolysis of $Fe(CO)_5$ in glacial acetic acid gives excellent yields of golden-yellow $Fe_2(CO)_9$, a compound having an Fe—Fe bond in addition to three bridging CO groups (49);[137,138]
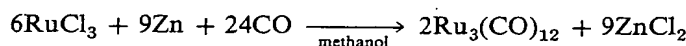
$$2Fe(CO)_5 \rightarrow CO +$$

49

and mild pyrolysis of this di-iron compound, or use of the following sequence of reactions, gives the greenish-black compound $Fe_3(CO)_{12}$.[139]

$$3Fe(CO)_5 + NR_3 + 2H_2O \rightarrow [R_3NH][HFe_3(CO)_{11}] + 2CO_2 + 2CO + H_2$$

$$12[R_3NH][HFe_3(CO)_{11}] + 18HCl \rightarrow 11Fe_3(CO)_{12} + 15H_2 + 3FeCl_2 + 12R_3NHCl$$

Numerous speculations on the structure of this molecule fill the literature. However, the correct structure was finally obtained in 1966, and, not surprisingly, it displays the triangular arrangement that is now known to be most favored by three metal atoms (50).[140]

50    $Fe_3(CO)_{12}$
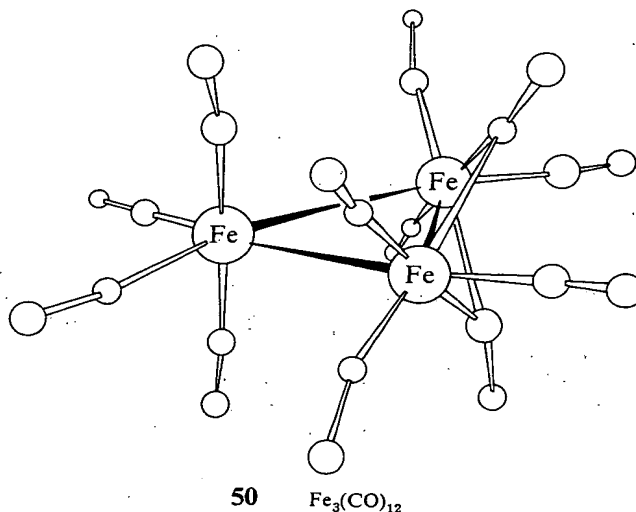
Reductive carbonylation of $RuCl_3$ gives $Ru_3(CO)_{12}$,[141]

$$6RuCl_3 + 9Zn + 24CO \xrightarrow[\text{methanol}]{} 2Ru_3(CO)_{12} + 9ZnCl_2$$

the structure of which is similar to that of its iron analog *except* that there are no bridging CO groups (51).

[137] W. L. Jolly, "The Synthesis and Characterization of Inorganic Compounds," Prentice-Hall, Englewood Cliffs, N.J. (1970), p. 472.

[138] R. B. King, "Organometallic Syntheses, Volume 1, Transition Metal Compounds," Academic Press, New York (1965), pp. 93–98.

[139] W. McFarlane and G. Wilkinson, *Inorg. Syn.*, **8**, 181 (1966).

[140] F. A. Cotton, *Prog. Inorg. Chem.*, **21**, 1 (1976); see also C. H. Wei and L. F. Dahl, *J. Amer. Chem. Soc.*, **88**, 1821 (1966).

[141] M. I. Bruce and F. G. A. Stone, *J. Chem. Soc. (A)*, 1238 (1967).
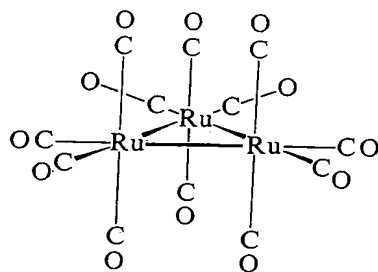
51

This change is illustrative of a central feature in metal carbonyl cluster chemistry—in general, bridging becomes less prevalent down a group. Further, the colors of the $M_3(CO)_{12}$ compounds—Fe, greenish-black; Ru, orange; and Os, yellow—illustrate the trend to less deeply colored compounds with heavier metals. Finally, owing to weaker core and ligand-ligand repulsions, the Ru and Os clusters are more strongly bonded than the iron cluster and, therefore, less easily broken down in chemical reactions. For example,[142]
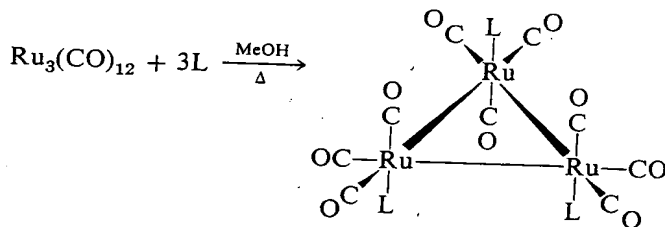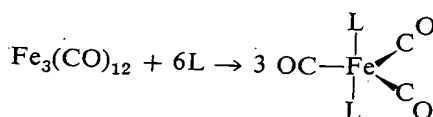
$$L = Ph_3P,\ Et_3P$$

From the discussion above, and the literature, another generalization can be made: for low valent metals in particular, three-metal-atom clusters are stable if they have a total of 48 valence electrons ($= 3 \times 16$) supplied by the three metals and their ligands. That is, if we count up the total number of electrons supplied by the ligands, divide by the number of metal atoms, and then add to the quotient the number of electrons supplied by the metal, the total should be 16 for a metal in a triangular cluster. The favorable "effective atomic number" of 18 may be gained by requiring each metal to form two metal-metal bonds. This analysis is outlined in Table 18-6 along with those for tetrahedral and octahedral clusters. In general, the electron counting rule works well, except for six-atom clusters; the latter will require molecular orbital methods, as seen below.

FOUR-ATOM, TETRAHEDRAL CLUSTERS

Clusters having four, five, or six vertices represent some of the most interesting cluster species, and research in this area is quite active, partly because it is thought

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[142] F. Piacenti, M. Bianchi, E. Benedetti, and G. Braca, *Inorg. Chem.*, **7**, 1815 (1968).

TABLE 18–6

ELECTRON COUNTING IN METAL CLUSTERS

Compound	Structure	Total Number of Valence Electrons (CO + M)	Electrons per Metal Atom	Number of M—M Bonds per M Atom Required to give EAN = 18
$Cr(CO)_6$	octahedron	$12 + 6 = 18$	18	0
$Mn_2(CO)_{10}$	two octahedra connected by Mn—Mn bond	$20 + 14 = 34$	17	1
$Fe_3(CO)_{12}$	structure **50**	$24 + 24 = 48$	16	2
$Co_4(CO)_{12}$	tetrahedron (structure **53**)	$24 + 36 = 60$	15	3
$[Co_6(CO)_{14}]^{4-}$	octahedron (structure **60**)	$28 + 54 + 4 = 86$	14.33	(see text)

that such clusters may resemble metals themselves and thereby offer an opportunity to study, after a fashion, reactions at metal surfaces.[143]

If $Fe(CO)_5$ is heated with dicyclopentadiene for several hours, an excellent yield of the purple metal-metal bonded compound $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ is obtained (Figure 18–17). However, if this compound is refluxed for an additional two weeks(!), the green-black tetrahedral cluster $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4$ (**52**) is obtained,[144] and this compound has several interesting features that can be used to illustrate general aspects of metal clusters.
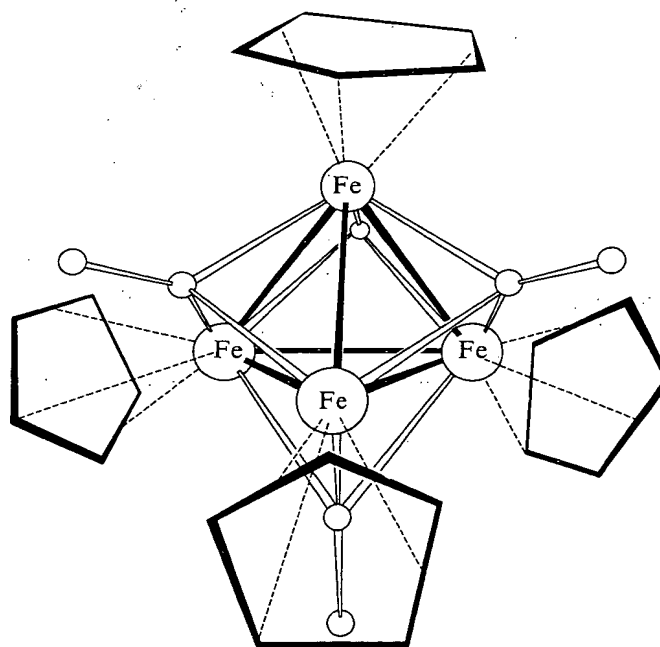
52 $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4$

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[143] M. Primet, J. M. Basset, E. Garbowski, and M. V. Mathieu, *J. Amer. Chem. Soc.*, **97**, 3655 (1975); H. D. Kaesz, *Chemistry in Britain*, **9**, 344 (1972).
[144] R. B. King, *Inorg. Chem.*, **5**, 2227 (1966).

Figure 18–18. Cyclic voltammogram of $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4$ in acetonitrile; 0.1 M tetrabutyl-ammonium hexafluorophosphate used as supporting electrolyte. Potentials measured at a Pt electrode *vs.* a saturated sodium chloride calomel electrode. [Reprinted with permission from J. A. Ferguson and T. J. Meyer, *J. Amer. Chem. Soc.*, 94, 3409 (1972). Copyright by the American Chemical Society.]
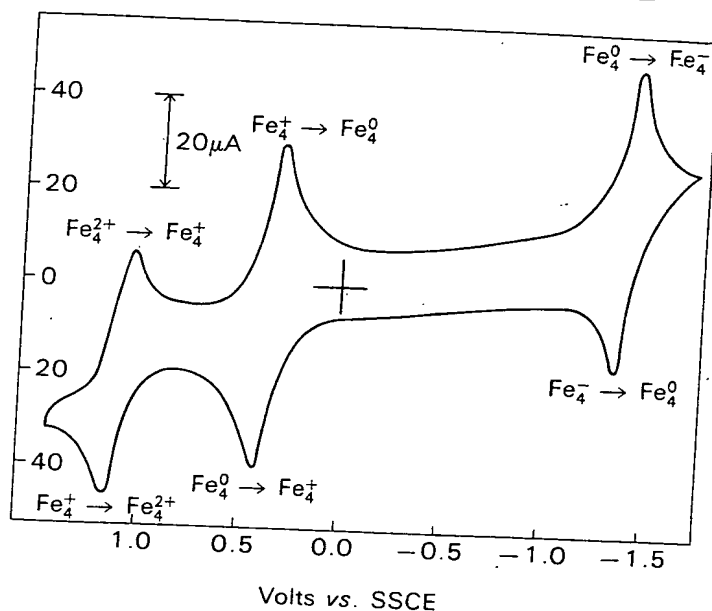
The electronic properties of compounds can often be probed by examining their electrochemical properties. One electrochemical technique that is particularly useful in this regard is cyclic voltammetry.[145] The cyclic voltammogram of **52** is illustrated in Figure 18–18, and it clearly shows that four molecular oxidation states (2+, 1+, 0, and 1−) are reversibly accessible for the cluster.[146] The accessibility of these states, and their apparent stability, suggests that the bonding in this cluster is quite delocalized, in spite of the fact that the 18 electron rule can be satisfied by assuming localized Fe—Fe single bonds along each tetrahedral edge. Delocalization of bonding electrons is further suggested by the fact that *all* of the Fe—Fe distances shorten slightly on going to the 1+ cluster.[147,148] This shortening suggests that the electron is removed

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[145] In cyclic voltammetry, the potential of an electrode in an unstirred solution is scanned from an initial value to a second value and back to the first to constitute a cycle. If an electroactive species is present in the solution, current will flow as the potential for reduction (or oxidation) is approached and will increase until the concentration of electroactive species in the immediate vicinity of the electrode is depleted. At this point the current drops to a constant value that is maintained by diffusion of the electroactive species from the bulk solution. A plot of current *vs.* potential shows a peak for this process. If the electron transfer process is reversible, the product from the initial electron transfer will also be electroactive and will undergo oxidation (or reduction) on the return sweep. The cyclic voltammogram will resemble one of the coupled peaks of Figure 18–18. For a thermodynamically reversible process, the current flowing on oxidation is equal to that flowing on reduction, and the average of the two peak potentials is the electrode potential for the process. If the product of the electron transfer is not stable, it may decompose to an electroinactive species or to another electroactive species; the shape of the cyclic voltammogram will reflect this.

Although cyclic voltammetry is frequently employed to determine reversibility of an electron transfer process, the technique has also been used in studies of the rate and mechanism of electron transfer and subsequent reactions of oxidized and reduced species. For further information on cyclic voltammetry and other electrochemical techniques of value to the inorganic chemist, see:

a. D. T. Sawyer and J. L. Roberts, Jr., "Experimental Electrochemistry for Chemists," Wiley-Interscience, New York (1974).

b. J. B. Headridge, "Electrochemical Techniques for Inorganic Chemists," Academic Press, New York (1969).

[146] J. A. Ferguson and T. J. Meyer, *J. Amer. Chem. Soc.*, 94, 3409 (1972); T. J. Meyer, *Prog. Inorg. Chem.*, 19, 1 (1975).

[147] M. A. Neuman, Trinh-Toan, and L. F. Dahl, *J. Amer. Chem. Soc.*, 94, 3383 (1972).

[148] Trinh-Toan, W. P. Fehlhammer, and L. F. Dahl, *J. Amer. Chem. Soc.*, 94, 3389 (1972).

from an mo that is essentially non-bonding or weakly antibonding, a suggestion confirmed by a simple mo approach.[147-149]

One other feature of $[(\eta^5-C_5H_5)Fe(CO)]_4$ is the triply bridging CO group, a form of bonding often found in metal cluster chemistry. As is usual for bridging CO ligands (Chapter 16), the more metals with which a CO group interacts, the lower will be the range within which the CO stretching frequency is found. In this particular case of **52**, ν_{CO} is 1620 cm^{-1}, one of the lowest ever observed.

Cobalt, rhodium, and iridium form a structural well-defined series of compounds with the general formula $M_4(CO)_{12}$.[150] This series also illustrates some general features of cluster chemistry. The black cobalt cluster **53** can be prepared by warming (slightly above room temperature) the commercially available, red, metal-metal bonded dimer $Co_2(CO)_8$. You will recall from Chapter 16 that the color change from red to black is typical of metal carbonyls: the greater the number of metals in the molecule, the deeper the color.

$$2\,Co_2(CO)_8 \xrightarrow[-4CO]{\Delta}$$

53 $Co_4(CO)_{12}$
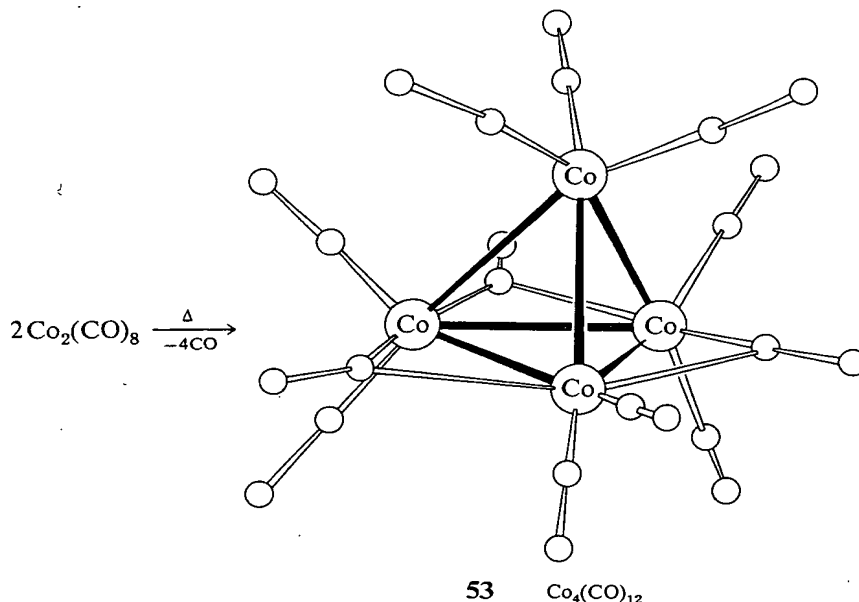
The kinetics of the thermolysis of $Co_2(CO)_8$ have been studied, and the rate law suggests that the coordinatively unsaturated species $Co_2(CO)_6$ is formed rapidly by loss of CO from $Co_2(CO)_8$, and then, in a slow step, $Co_2(CO)_6$ dimerizes to the observed cluster.

Red $Rh_4(CO)_{12}$ or yellow $Ir_4(CO)_{12}$ can be made by reductive carbonylation reactions such as

$$RhCl_3 \cdot xH_2O \xrightarrow{CO} [Rh(CO)_2Cl]_2 \xrightarrow[Cu]{CO,\ 200\ atm} Rh_4(CO)_{12}$$
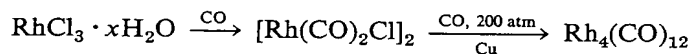
As was also pointed out above, it is another characteristic of metal clusters that those of the first transition series are most deeply colored. In changing from black (Co) to red (Rh) or yellow (Ir), the $M_4(CO)_{12}$ series again illustrates this trend.

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[149]This mo treatment is essentially confirmed by a recent Mössbauer study of the neutral and 1+ $[(\eta^5-C_5H_5)Fe(CO)]_4$ clusters. R. B. Frankel, W. M. Reiff, T. J. Meyer, and J. L. Cramer, *Inorg. Chem.,* **13,** 2515 (1974).

[150]See ref. 116.

The three $M_4(CO)_{12}$ clusters are based on the tetrahedron, and, assuming localized electron-pair M—M bonds along each edge, each metal atom obeys the 18 electron rule. However, the CO ligands are arranged differently in the iridium cluster than in the cobalt or rhodium clusters. While there are nine terminal and three bridging CO's in the cobalt and rhodium clusters, all CO's are terminal in the iridium compound (54). This is another example of a general feature of metal carbonyls: within a related series, compounds of the heavier metals have fewer bridging CO's than those of the lighter metals.
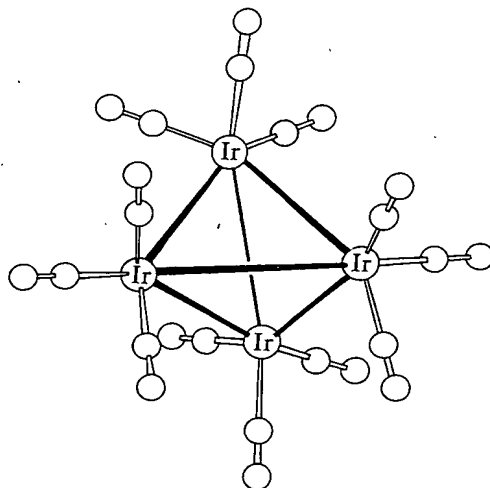
54 $Ir_4(CO)_{12}$

Just as in borane chemistry, one can remove a vertex from a metal cluster and replace it with another group as long as the replacement contributes a sufficient number of electrons and orbitals of appropriate symmetry. Therefore, it is not surprising that a $Co(CO)_3$ vertex in $Co_4(CO)_{12}$ can be replaced by a $\overset{\displaystyle Y}{\underset{\diagdown}{\underset{|}{\overset{|}{C}}}}$ to give $Y-CCo_3(CO)_9$ (55).
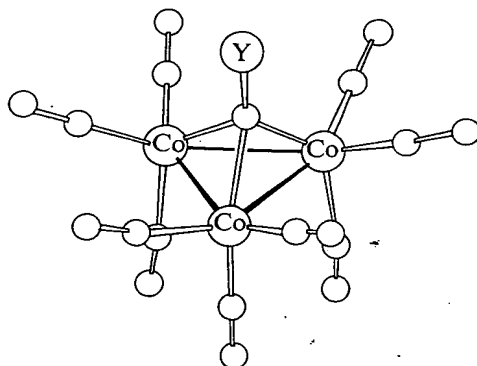
55 $Y-CCo_3(CO)_9$

Y = H, halide, or organic group

Although the CO ligands play a slightly different role in 55 than in $Co_4(CO)_{12}$, each vertex again obeys the inert gas rule. These alkylidynetricobalt nonacarbonyl clusters

represent a large and thoroughly studied class of organometallic compounds.[151] Many can be prepared in high yield by reaction of $Co_2(CO)_8$ with geminal trihalides such as $Cl—CCl_3$ and $Cl_3C—COOR$.[152]

$$Co_2(CO)_8 + Cl_3C—R \rightarrow R—CCo_3(CO)_9$$
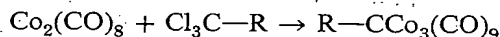
The resulting CCo_3 cage complexes are usually quite stable to atmospheric oxidation and the compounds are highly colored, most often purple or deep brown-purple. The cage is generally considered electron-withdrawing with respect to the apical Y group, and, as in **52**, there is experimental evidence for electron delocalization within the cage.[152a]

The reactions of the apical carbon in **55**, and of groups attached to it, are certainly not ordinary, as they are strongly influenced by the severe stereochemical constraints arising from the equatorial CO groups that make flank-side attack difficult; backside attack at the apical carbon is, of course, impossible. In fact, it is apparently because of these stereochemical constraints that the simple acid-catalyzed hydrolysis of $(OC)_9Co_3C—COOR$ esters does not occur. Instead, hydrolysis to give $(OC)_9Co_3C—COOH$ may be accomplished only by dissolving the purple ester in concentrated sulfuric acid.[153] By analogy with the known organic chemistry of highly hindered carboxylic acids, it is presumed that this reaction proceeds through an intermediate acylium ion, $(OC)_9Co_3C—C≡O^+$. This fact was substantiated by the finding that the acylium ion (after having been isolated in the form of its PF_6^- salt) could react with a host of different nucleophiles (among them water to give the carboxylic acid), as shown below.[154]
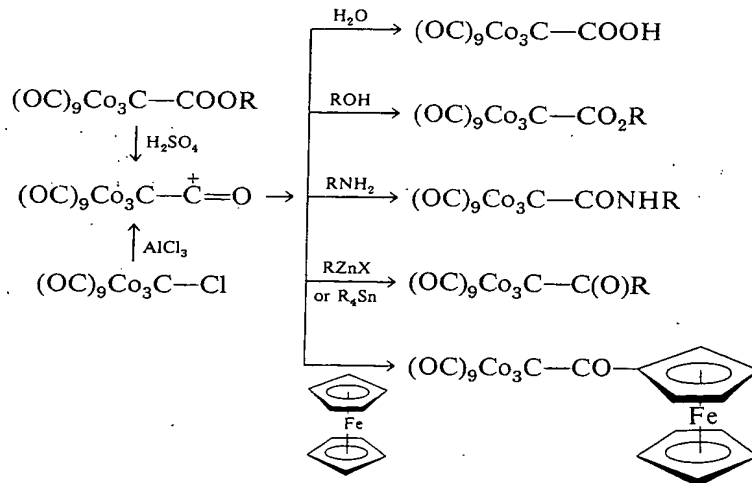
FIVE- AND SIX-ATOM CLUSTERS

Numerous clusters containing five or more metal atoms in the cage are known. For example, there are more than 50 clusters based on metal carbonyls: neutral

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[151] See ref. 122.

[152] D. Seyferth, J. E. Hallgren, and P. L. K. Hung, *J. Organometal. Chem.*, **50**, 265 (1973). It is unfortunate that the mechanism of this interesting synthesis is not yet known.

[152a] J. Kotz, J. V. Petersen, and R. C. Reed, *J. Organometal. Chem.*, **120**, 433 (1976).

[153] D. Seyferth, J. E. Hallgren, and C. S. Eschbach, *J. Amer. Chem. Soc.*, **96**, 1730 (1974).

[154] The acylium ion may also be generated by reaction of the readily available $(OC)_9Co_3C—Cl$ with $AlCl_3$. D. Seyferth and G. A. Williams, *J. Organometal. Chem.*, **38**, C11 (1972).

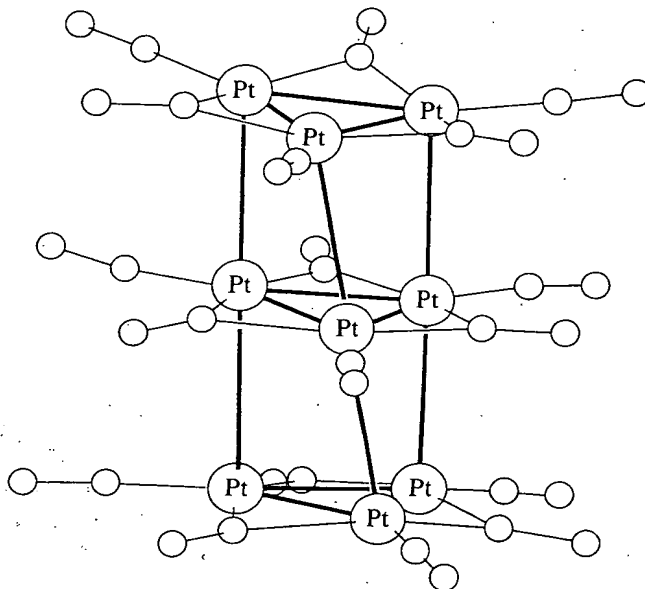compounds (56), anions (57 and 58), carbides (59), and hydrides [*e.g.*, $H_2Rh_6(CO)_{18}$].
All of the clusters of this type contain Group VIII metals.
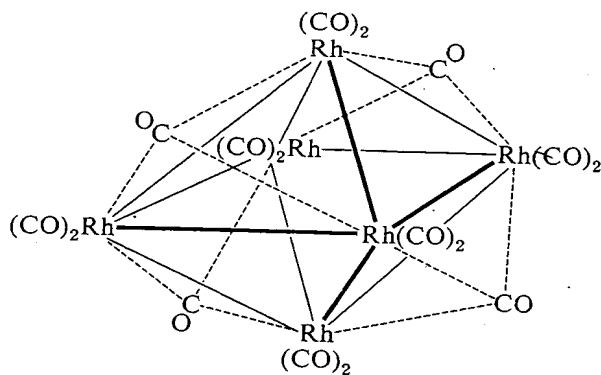
56 $Rh_6(CO)_{16}$
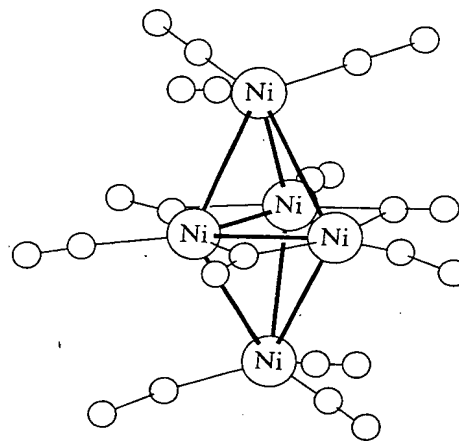
**57**[155] $[Ni_5(CO)_9(\mu_2\text{-}CO)_3]^{2-}$ (C_{3v})


58[155] $[Pt_9(CO)_9(\mu_2\text{-}CO)_9]^{2-}$ (D_3)

[155] The symbol μ designates a bridging ligand, and the subscript indicates the number of metal atoms bridged.
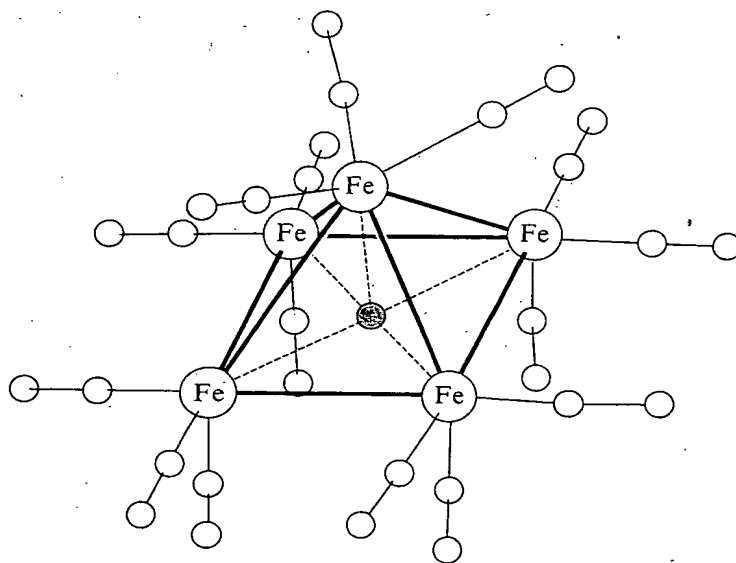
59 $Fe_5(CO)_{15}C$

Cobalt carbonyl clusters are among the more thoroughly studied of the larger clusters. As seen in the following scheme, a key species is the yellow-green anion $[Co_6(CO)_{15}]^{2-}$. This anion can be obtained by reduction of the previously discussed $Co_4(CO)_{12}$ cluster (53) or better by heating an ethanolic solution of $[Co(EtOH)_x][Co(CO)_4]_2$ *in vacuo*. Reduction of the $[Co_6(CO)_{15}]^{2-}$ anion or direct reduction of $Co_4(CO)_{12}$ gives the deep red species $[Co_6(CO)_{14}]^{4-}$ (60).[156]
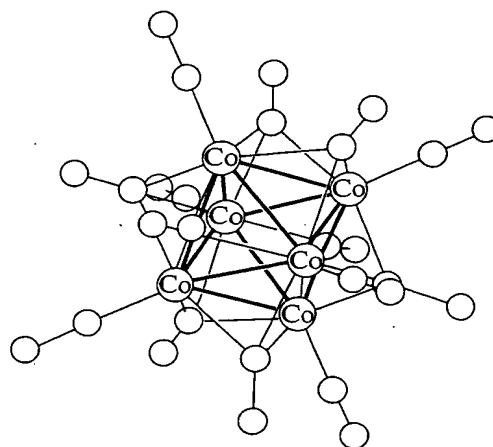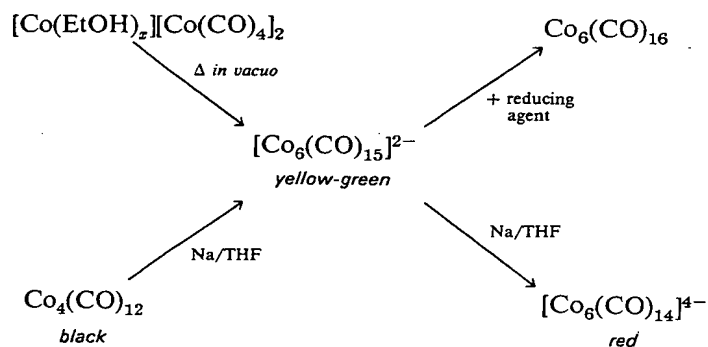
60 $[Co_6(CO)_6\mu_3\text{-}CO)_8]^{4-}$ (S_6)

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[156]See ref. 118.

The mode of bonding in clusters such as $[Co_6(CO)_{14}]^{4-}$ has attracted considerable interest.[157] As indicated in Table 18-6, M_3 clusters are characterized by 48 total valence electrons, and bonding can be adequately represented by localized electron pair bonds between metals. The same is true of M_4 clusters, where there are 60 valence electrons. In $[Co_6(CO)_{14}]^{4-}$, however, a total of 86 electrons is contributed by the metal atoms, the CO's, and the charge. Were the "edge-bond" description possible for this compound as for $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4$ or $Co_4(CO)_{12}$, only 84 electrons would be necessary.[158] To account for this discrepancy, Wade has suggested that bonding within the cage is quite delocalized and is formally analogous to that of the stoichiometrically equivalent borane compounds.[159] In the present case, $[Co_6(CO)_{14}]^{4-}$ (or written alternatively as $[(CoCO)_6(CO)_8]^{4-})$ is equivalent to $(BH)_6^{2-}$, the molecular orbital diagram for which was presented in Figure 18–9. A very similar mo scheme can be built for the cobalt cluster by recognizing that the Co $d\sigma$ ao is analogous to the *endo* hao of each boron, and the Co $d\pi$ ao's replace the $p\pi$'s of boron.

M_6 $d\sigma$ ao   like B_6 $p\sigma$ hao

M_6 $d\pi$ ao   like B_6 $p\pi$ ao
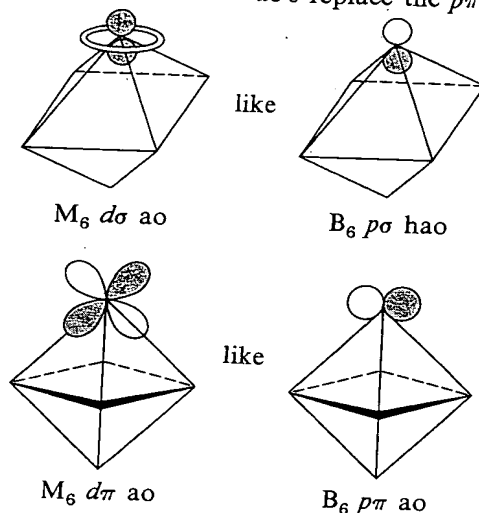
In both $(BH)_6^{2-}$ and $[Co_6(CO)_{14}]^{4-}$, M_6 cage bonding is determined by seven occupied, strongly bonding mo's $[a_{1g}(\sigma) + t_{2g}(\pi) + t_{1u}(\pi)]$ and not by 12, as required by the "edge-bond" description. The bonding of the 14 CO ligands implies, as in Figure 18–9, the stabilization of the 14 electron pairs in the CO σ TASO's. Thus, M_6 and CO bonding account for 21 of the 43 valence pairs associated with the cage. The remaining 22 pairs ($3\frac{2}{3}$ per cobalt) apparently fill cage non-bonding mo's stabilized by cage-CO π retrobonding. Accordingly, the "EAN" of each cobalt is just $14\frac{1}{3}$ ($= 86/6$). This same analysis is true for $[Ru_6(CO)_{18}]^{2-}$, which is isoelectronic with $[Co_6(CO)_{14}]^{4-}$. In the case of the ruthenium compound there are again seven cage bond pairs, 18 CO σ bond pairs, and 18 "non-bonding" pairs (three per Ru) for an "EAN" of $14\frac{1}{3}$ again. In both the Co and Ru clusters, the failure of the usual two-center electron pair bond concept to account for M—M bonding causes the breakdown of the 18 electron rule. Finally, note that the discrepancy between the prediction of the 18 electron rule and the observed electron count amounts to a deficiency of $3\frac{2}{3}$ electrons per metal—not an excess of 1/3 as implied by the "edge-bond" counting procedure.
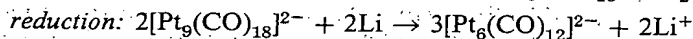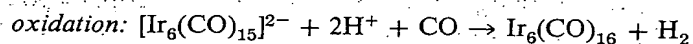
[157] D. M. P. Mingos, *J. C. S. Dalton*, 133 (1974).
[158] The need for 84 electrons is arrived at as follows: If each Co is to have an EAN of 18 electrons, and edge-bonding is to exist, the nine electrons of each Co must be supplemented by four electrons from M—M bonds to nearest neighbors, by two electrons from a bond to a terminal CO, by two and two-thirds electrons from the four triply bridging CO's that each cobalt shares with its four nearest neighbors, and by one-third of an extra electron per Co for a cluster charge of 2−. That is, the formula of the cluster should be $[Co_6(CO)_{14}]^{2-}$, an anion having a total of 84 electrons.
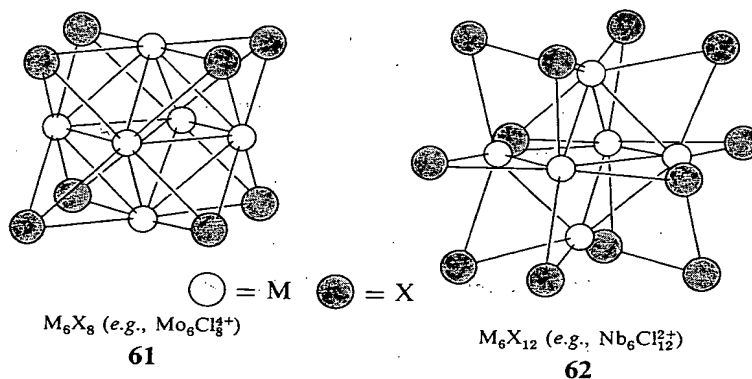[159] K. Wade, *Chem. Britain*, 11, 177 (1975); *Adv. Inorg. Chem. Radiochem.*, 18, 1 (1976).

Although it is accelerating because of interest in the area, the publication of research on metal clusters is slow. This is largely due to the difficulty of the synthesis, separation, and structural characterization of clusters. Thus, relatively little has yet been done in a systematic way regarding their chemistry, aside from examination of such basic processes as[160]

oxidation: $[Ir_6(CO)_{15}]^{2-} + 2H^+ + CO \rightarrow Ir_6(CO)_{16} + H_2$

reduction: $2[Pt_9(CO)_{18}]^{2-} + 2Li \rightarrow 3[Pt_6(CO)_{12}]^{2-} + 2Li^+$

ligand substitution (which frequently occurs with cage degradation):

$$Rh_6(CO)_{16} + 12PPh_3 \xrightarrow[C_6H_6]{25°C} 3[Rh(CO)_2(PPh_3)_2]_2 + 4CO$$
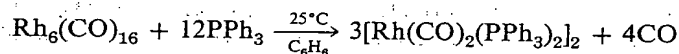
Just as the heavier metals at the left of the transition metal series form binuclear halide complexes with metal-metal bonds, these same metals form larger clusters. Two of the best known are those based on the octahedron: $[Mo_6Cl_8]^{4+}$ **(61)**[161] and $[M_6X_{12}]^{n+}$ (M = Nb, Ta; X = F, Cl, I; n = 2,3,4) **(62)**.[162,163]

$\bigcirc$ = M   ⬤ = X

M_6X_8 (*e.g.,* $Mo_6Cl_8^{4+}$)
61

M_6X_{12} (*e.g.,* $Nb_6Cl_{12}^{2+}$)
62

These also present a problem regarding a description of their bonding. If the halide ions are removed from the clusters, a core of the type Mo_6^{12+} or Nb_6^{14+} remains. In the case of Mo_6^{12+}, the cluster is composed of Mo^{2+} ions just as in $[Mo_2Cl_8]^{4-}$, which was discussed earlier. This means that there are $6 \times 4 = 24$ electrons available for cluster bonding in Mo_6^{12+}; if all 12 pairs occupy bonding mo's, there is a net of one electron pair for each Mo—Mo pair, and each Mo may be considered to be bonded to its four nearest neighbors by localized two-electron bonds. In the Nb_6^{14+} core, however, there are $6 \times 5 - 14 = 16$ electrons or only eight pairs for cage bonding. Thus, as in $[Co_6(CO)_{14}]^{4-}$, there is a deficiency of electrons and an "edge-bond" description is not appropriate. It is best to resort again to mo methods.

A more detailed mo approach to bonding in M_6 clusters such as $[Nb_6Cl_{12}]^{2+}$ is outlined in an Appendix to this chapter. The most important result of this approach is that $d\delta$ ao's are present at each vertex (**63** and **64**). That is, metal $d_{x^2-y^2}$

d_{xy}
63

views of M_6 cluster from a vertex

$d_{x^2-y^2}$
64
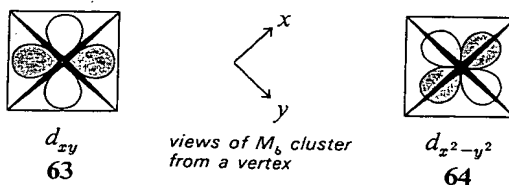
[160] See ref. 118.
[161] J. C. Sheldon, *J. Chem. Soc.,* 1007, 3106 (1960).
[162] F. W. Koknat and R. E. McCarley, *Inorg. Chem.,* **13**, 295 (1974).
[163] B. G. Hughes, J. L. Meyer, P. B. Fleming, and R. E. McCarley, *Inorg. Chem.,* **9**, 1343 (1970).

ao's lie so that their lobes extend over octahedral edges, while metal d_{xy} lobes extend over octahedral faces. In the $[Mo_6Cl_8]^{4+}$ case, the last six electrons of the 12 cage bonding electron pairs are accommodated in a t_{2u}^6 mo composed of $d_{x^2-y^2}$ orbitals, and the mo's arising from the d_{xy} orbitals are unused. It is for this reason that eight Cl^- ions are associated with the Mo_6^{12+} core and that these Cl^- ions are located at the faces where the Cl^- electron pairs can overlap the empty d_{xy} mo's! On the other hand, the $[Nb_6Cl_{12}]^{2+}$ cluster has eight cage electron pairs, and the last pair enters an a_{2u}^6 mo composed of d_{xy} ao's; the $d_{x^2-y^2}$ mo's, lying along octahedral edges, are unused. Therefore, there are $12Cl^-$ ions bridging the 12 octahedral edges where they can effectively interact with the empty $d_{x^2-y^2}$ mo's.

---

20. Unlike clusters with six metal atoms, compound **65** (p. 1046) with a cube of metal atoms obeys the 18 electron rule. Verify that this is indeed the case and that localized, two-electron bonds can be postulated between adjacent nickel atoms.

21. By reference to the 18 electron rule, verify the fact that it is necessary to postulate a Cr—Cr triple bond in **43** if the compound is to be diamagnetic.

22. Suggest a way to form W—SnR$_3$, W—GeR$_3$, or W—PbR$_3$ bonds if the starting materials are the tungsten compound below and a suitable germanium, tin, or lead compound.
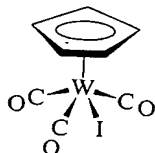
[If you need a hint, see T. A. George and C. D. Sterner, *Inorg. Chem.*, **15**, 165 (1976).]

23. What is the most likely order for the Mo—Mo bond in the ion $[Mo_2(CH_3)_8]^{4-}$? Sketch a possible structure of the ion.

24. Two of the best characterized metal-metal bonded compounds are $Mo_2(CH_2SiMe_3)_6$ and $Mo_2(NMe_2)_6$. What is the Mo—Mo bond order in these two compounds? Sketch possible structures for the molecules.


EPILOG

This discussion of the structure, bonding, and reactivity of boron hydrides and metal clusters was intended to be an overview; as such, it is far from a complete treatment of an area that promises to be one of increasing importance in the next few years. The discovery of metalloboranes has led to a resurgence of interest in boron hydride chemistry, and, as metalloboranes show promise as catalysts,[164] research in this area is certain to continue.

As the structural chemistry of metal clusters becomes better understood one can expect more attempts at their deliberate synthesis, with increasing probability of success.[164a] The recent synthesis of $Ni_8(CO)_8(\mu_4\text{-PPH})_6$ (**65**) is a case in point.[165] Finally,

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[164] T. E. Paxson and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **96**, 4676 (1974); E. H. S. Wong and M. F. Hawthorne, *Chem. Commun.*, 257 (1976).
[164a] For example, see G. L. Geoffroy and W. L. Gladfelter, *J. Amer. Chem. Soc.*, **99**, 304 (1977).
[165] L. D. Lower and L. F. Dahl, *J. Amer. Chem. Soc.*, **98**, 5046 (1976).

we would emphasize that we have by no means covered the topic of molecular polyhedra completely. Perhaps arbitrarily, we have chosen to restrict ourselves to those compounds in which metal-metal bonding is a virtual certainty. However, there are many other molecular polyhedra that do not involve metal-metal bonding and yet have interesting and important properties. For example, compound **66** has been described as a model for iron-sulfur proteins, and it will be discussed in considerably more detail in the next chapter on biochemical aspects of inorganic chemistry.

In general, it is certain that molecular polyhedra will come more and more to the attention of the chemical community as practical uses for them continue to be found.

65 $Ni_8(CO)_8(\mu_4\text{-}PC_6H_5)_6$

66 $[Fe_4S_4(SC_6H_5)_4]^{2-}$

10^{18}
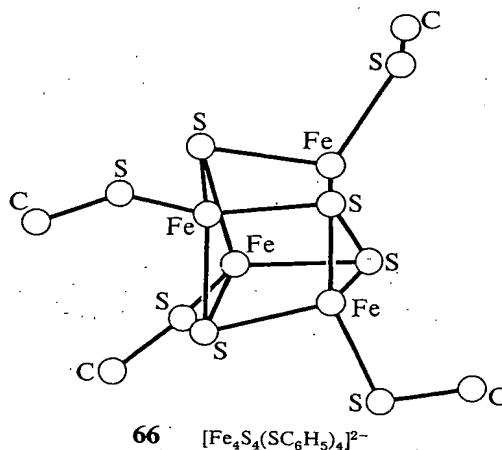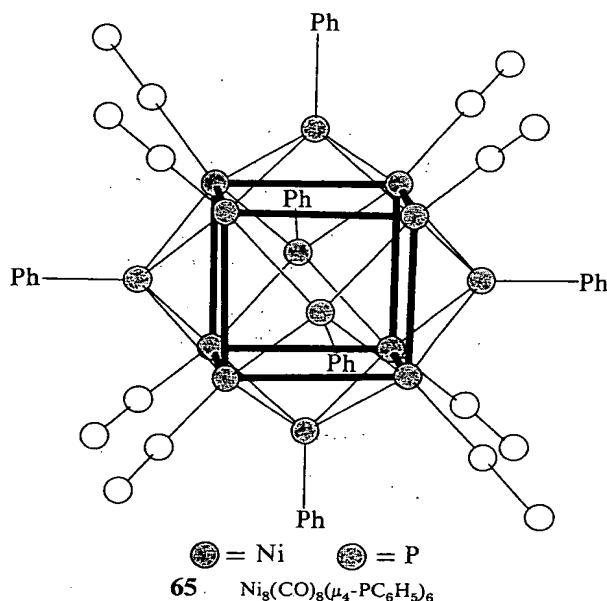
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